# A Study of the Photovoltaic Effect for Metallic Electrodes in Aqueous and Liquid Ammonia Solutions of their Ions

*By*

G. H. KISSIN

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
AT THE UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
JUNE 1944

# ELECTRON EMISSION AND THE PHOTOVOLTAIC EFFECT

## Study of the Photovoltaic Effect for the Electrode: Solution of Sodium in Liquid Ammonia[1]


ABSTRACT

The role of electron emission in modern theories of cation deposition and electrode potential phenomena is discussed, and the possible relationship between photopotentials and the energy of electron emission from electrodes immersed in electrolytic solution is defined. An electrode system, comprising a metallic solution of sodium in liquid ammonia, was established by means of which the validity of the electron emission or photoelectric theory of the photovoltaic effect for metallic electrodes could be experimentally tested. No observable photovoltaic effect was obtained for the sodium in liquid ammonia electrode, a system which is known to emit electrons when illuminated, and it is therefore concluded that photoelectric emission alone is not a sufficient condition for the generation of photovoltaic effects for metals in contact with solutions of their ions.


---

### INTRODUCTION

Whenever current passes through an electrolytic system, whether it is a primary or an electrolytic cell, chemical reactions involving electrons take place at the electrodes. Several theories have been proposed to explain the precise mechanism of these electron reactions; but the situation is still in a highly unsatisfactory state. For the simple case of the partial or total discharge of a positive ion at the cathode, by some means the electron in the metal and the positive ion in the solution must get together. In any case the electron must be removed from the metal and this requires energy. It is well known, also, that under the proper conditions, light energy may be used to remove electrons from metal surfaces. It would appear likely that there should be some relation, and that a fairly close one, between the light energy required to remove the electron and the energy involved in the discharge of a positive ion during electrolysis. Or,


R. UNIV.
BIBLIOTHEEK
LEIDEN

in other words, between the so-called "work function" and the electrode potentials.

In recent years a proper understanding of the mechanism of the photovoltaic effect has assumed new importance because of its bearing on the theories of electrode phenomena developed by Gurney[4] and Butler.[5] An important concept in the Gurney-Butler theory is the work function of electrons in metals. The work function is defined as the energy required to remove an electron from the metal into a vacuum. If the potential change obtained upon illumination of a metallic electrode in a solution containing its ions is caused by emission of electrons, then a quantitative investigation of this photovoltaic effect should give information concerning the magnitude of work functions of metallic electrodes *in solutions of their ions.* The work necessary to remove an electron from a metal *in vacuo* can be determined from measurements of the photoelectric threshold. To calculate the corresponding work function, for a metal *in a solution of its ions,* from threshold measurements of the photovoltaic effect under such conditions necessitates the assumption that the photopotentials have their origin primarily in electron emission. Work functions have meaning only if electrons are actually liberated from the metal by the action of some form of energy, in this case, light. If the potential changes in the photovoltaic effect have their origin in some phenomenon other than electron emission, then the particular quantity of energy known as the work function does not play a part in the electrode process, and cannot be determined from experiments on the photovoltaic effect. A survey of the literature indicates that, in the case of metallic electrodes at least, the consensus of the opinion is that the photovolaic effect is an electron emission phenomenon.

The present work was undertaken in order to determine whether or not the electron emission mechanism could be demonstrated experimentally as a primary cause of the photovoltaic effect for a metallic electrode in a solution of its ions, and thus relate the energy of ion discharge in electrolysis with the energy of liberation of electrons from the metal into a vacuum.

It was considered that a study of photovoltaic effects for an electrode system which is definitely known to emit electrons when illuminated with light of suitable frequency should be a logical method of approach.

Gibney and Dole[6] investigated the photovoltaic effect of the following cell on the basis that, if a true electron emission effect existed for the boundary metal-solution, it would be much more pronounced for active metals with low work functions than for the relatively inert metals having high work functions:

$$\mathrm{Na} \mid \mathrm{NaI\ in\ dry\ } C_5H_{11}NH_2 \mid \mathrm{Na}.$$

One sodium electrode was illuminated and the other dark. The source of illumination was unresolved radiation from a pyrex mercury arc lamp. No measurable photovoltaic effect was ever observed for a perfectly dry cell in which the sodium surface was apparently clean.

[4] R. W. Gurney, "Ions in Solution", University Press, Cambridge (1936).
[5] J. A. W. Butler, "Electrocapillarity", Chemical Publishing Co., New York (1940).
[6] R. B. Gibney and M. Dole, J. Chem. Phys. **4**, 653 (1936).

The classical researches of Kraus[7] and collaborators have established that, in the conduction of electricity by solutions of the alkali metals in liquid ammonia, the current is carried jointly by the positive ions of the metal and negative electrons. In a solution of sodium in liquid ammonia there exist the following equilibria:

$$Na \rightleftarrows Na^+ + e^-$$
$$e^- + xNH_3 \rightleftarrows e(NH_3)\ x$$

From measurements of the e.m.f. of concentration cells of sodium in liquid ammonia Kraus[8] determined the transference numbers of the positive and negative carriers. The facts obtained led Kraus to assume that at high concentration a considerable number of electrons become unsolvated and behave in the same way as "free" electrons in metals.

Further evidence of the metallic nature of these solutions comes from the investigation by Kraus and Lucasse[9] of the temperature coefficient of conductance of solutions of sodium in liquid ammonia.

Greater insight into the metallic nature of solutions of sodium in liquid ammonia has been gained from recent work by Thode[10] and by Freed and Sugarman[11] on the magnetic susceptibilities of these solutions. The atomic susceptibility of liquid ammonia solutions of sodium in concentrations above 0.5 *N* is about the same as that of metallic sodium. As the concentration decreases below 0.5 *N* the atomic susceptibility increases in a manner which can be quantitatively predicted by the statistical mechanics of Fermi and Dirac for electrons in metals.

The existence of a photoelectric effect for lithium solutions in liquid ammonia was discovered by Kraus[12] who recorded the fact without undertaking further experimental work. Schmeing[13] and, independently, Häsing,[14] investigated the spectral sensitivity of the photoelectric effect, over a wide range of light frequencies, of solutions of sodium in liquid ammonia of several different concentrations. The photoelectric response, at all wave lengths, increases with the concentration, and the threshold wave length varies from about 7,000 Å for solutions of medium concentration to about 9,700 Å for solutions saturated. In conformity with the behavior of metals, temperature variation appears to have little effect on the photoelectric response of solutions of sodium in liquid ammonia. The studies of Schmeing and of Häsing show definitely that the photoelectric response of solutions of sodium in liquid ammonia is due to the emission of electrons from the solution.

It is apparent, from the properties which have been summarized above, that a solution of sodium in liquid ammonia is an ideal electrode for the purpose of testing the electron emission theory of the photovoltaic effect.

[7] C. A. Kraus, J. Franklin Inst. **212**, 537 (1931).
[8] C. A. Kraus, J. Am. Chem. Soc. **36**, 864 (1914).
[9] C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc. **44**, 1941 (1922).
[10] H. G. Thode, Ph. D. dissertation, University of Chicago (1934).
[11] S. Freed and N. Sugarman, J. Chem. Phys. **11**, 354 (1943).
[12] C. A. Kraus, J. Am. Chem. Soc. **43**, 749 (1921).
[13] G. M. Schmeing, Ph. D. dissertation, University of Chicago (1939).
[14] J. Häsing, Ann. Physik **37**, 509 (1940)

The solution emits electrons when illuminated with radiation of wave lengths ranging from about 3,000 Å to 9,000 Å. No photochemical process, which might effect the electrode potential, takes place in this region. From the presence or absence of a photovoltaic effect for an electrode of sodium in liquid ammonia, certain inferences may be made: (1) Any photovoltaic effect which might occur would appear to be due to the photoelectric emission of electrons; although an electrochemical mechanism, of the type proposed by Wildermann,[15] is not entirely ruled out. (2) On the other hand, if no photovoltaic effect is observed for such an electrode, it would seem conclusive that the photoelectric emission of electrons is not in itself a sufficient condition for the generation of a photovoltaic effect.

An answer to the implied questions above was sought through a study of the photovoltaic effect for the two cell systems:

*A.* Na in $NH_3$ (dark) | Na in $NH_3$ (illuminated)

*B.* Na in $NH_3$ (dark) | NaCl in $NH_3$ | Na in $NH_3$ (illuminated)

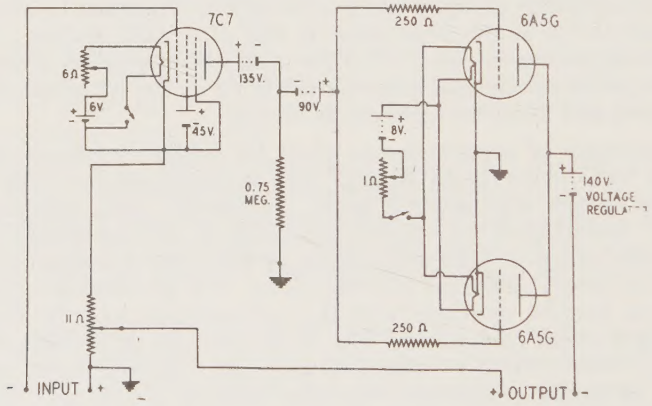


FIG. 1. D. C. amplifier circuit.

## EXPERIMENTAL

In this laboratory an oscillograph-amplifier system has been developed by Ferguson and collaborators. With this apparatus it is possible to obtain a continuous photographic record of potential changes in a voltaic or electrolytic cell. Variations taking place within a period of $10^{-4}$ seconds may be followed. The amplifier unit draws less than $10^{-9}$ amperes of current from the cell under investigation, thus avoiding errors due to polarization. A similar amplifier-oscillograph system, adapted for studies of the photovoltaic effect, was designed and constructed for this work.

[15] M. Wildermann, Phil. Trans. Roy. Soc. **A193**, 337 (1902); Phil. Mag. **5**, 203 (1903); Phil. Trans. Roy. Soc. **A206**, 355 (1906).

The oscillograph is a Westinghouse one-element simplified "Osiso", of the vibrator-galvanometer type. The oscillograph has an approximate sensitivity of one millimeter deflection at the focal plane per one milliampere current, and requires a current of 100 milliamperes for full scale deflection. The instrument is fitted with a slow speed camera taking a standard size roll film.

The direct current amplifier circuit, shown in Fig. 1, is a further development of the design worked out by Ferguson and collaborators[16]. Changes in the tubes and a new method of varying the amplifier sensitivity have resulted in a notable improvement in the stability of the output. The 7C7 tube, used in the first stage of amplification, is a high amplification factor, high grid-plate resistance tube, which requires less heater power and has better shielding properties than other tubes previously used in this circuit. Two 6A5 G tubes, operating in parallel, replace the single 2A3 formerly employed in the second stage of amplification. This permits high power output without overloading and greatly enhances the stability of the amplifier. The 11 ohm potentiometer between ground and the 7C7 cathode is a degenerating resistance, used to vary the sensitivity of the amplifier by the negative feedback method. The principles and applications of feedback in amplifiers have been discussed by Vance[17] and Black[18]. The feedback method is much simpler and gives steadier operation than the previous method of varying grid potentials to change amplifier sensitivity. Throughout this work the amplifier was operated in its highest sensitivity range. A potential change of 0.05 millivolt was detectable at this sensitivity.

Because of the large power requirement of the 6A5 G tubes, dry batteries are unsatisfactory as a "B" supply. A modification of the RCA Model TMV 118 B regulated power unit[19] was employed as power supply for the second amplification stage.

A Wolff potentiometer, in conjunction with a Leeds & Northrup thermionic amplifier, was used to measure the dark potential between the electrodes. The potentiometer was also employed in the calibration of the amplifier-oscillograph system.

The calibration and operation of the amplifier-oscillograph system has been described in previous publications from this laboratory.[16]

The technics for handling liquid ammonia solutions have been described by Johnson and Fernelius.[20] In this work the solutions were formed and manipulated at temperatures below the boiling point of liquid ammonia, thereby obviating the inconveniences of high pressure systems. The dry ice-alcohol mixture was used as refrigerant and all measurements are at the temperature of this mixture,—78° C.

The all glass photovoltaic cell vessel for the system and the glass system

$$\text{Na in } NH_3 \;\Big|\; \text{NaCl in } NH_3 \;\Big|\; \text{Na in } NH_3$$

for preparing solutions and filling the cell are shown diagrammatically in Fig. 2. The left hand vertical chamber of the cell holds the sodium in liquid ammonia solution which is protected from the light by a close

[16] A. L. Ferguson and H. Bandes, Trans. Electrochem. Soc. **81**, 273 (1942); A. L. Ferguson and M. B. Towns, Trans. Electrochem. Soc. **82**, 307 (1943).
[17] A. W. Vance, Rev. Sci. Inst. **7**, 489 (1936).
[18] H. S. Black, Bell Syst. Tech. J. **13**, 1 (1934).
[19] A. L. Ferguson and S. Kleinhexsel, J. Phys. Chem. **42**, 172 (1938).
[20] W. C. Johnson and W. C. Fernelius, J. Chem. Education **6**, 441 (1929).

fitting black fibre shield which is not shown. The sodium in liquid ammonia solution which is to be illuminated is contained in the chamber to the right. A pyrex optical flat (W), 1/16 in. (1.6 mm.) thick, is sealed in at the top of this chamber.

Electrical contact with the sodium in liquid ammonia electrodes is made with gray platinum wires sealed in through the sides of the chambers. The gray platinum was prepared by "platinizing" pure platinum wire with platinum black and then igniting the wire to white heat in a Meker flame. Burgess and Kahler,[21] in a study of the catalytic effect of various common metals upon the reaction reported that gray platinum prepared in

$$Na + NH_3 \rightarrow NaNH_2 + 1/2\ H_2$$

the above manner was one of the poorest catalysts. In this work, dry solutions of sodium in liquid ammonia remained stable for more than a week when stored over specimens of gray platinum.

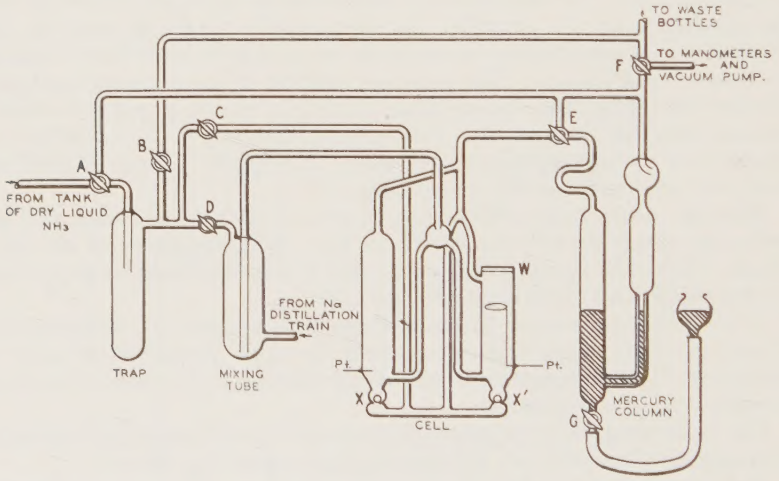


FIG. 2.. Apparatus for filling cell.

The lower cross tube connecting the end chambers serves as the container for the solution of sodium chloride in liquid ammonia. The glass beads (X and X′) at the bottom of each end chamber enable a sharp liquid junction to be formed between the solutions of sodium and sodium chloride. In actual practice the glass beads were quite effective in cutting down diffusion between the two solutions, several hours elapsing before the blue color of the sodium solution became discernable in the sodium chloride solution.

The cell designed for the electrode system has not been shown. It is

$$\text{Na in } NH_3 \text{ (dark)} \quad \Big| \quad \text{Na in } NH_3 \text{ (illuminated)}$$

[21] W. M. Burgess and H. L. Kahler, Jr., J. Am. Chem. Soc. **60**, 439 (1938).

similar to the one described above, differing only in the absence of the glass beads and in having a somewhat shorter and narrower connecting tube between the two end chambers.

The cells and mixing tube, Fig. 2, are detachable from the rest of the system by means of ground joints.

The operation of the system may best be described by outlining the procedure for an experimental run with the cell system

$$\text{Na} \mid \text{NaCl} \mid \text{Na}$$
$$(\text{all in liquid } NH_3)$$

A weighed quantity of dry fused sodium chloride is placed in the bottom cross tube of the photovoltaic cell vessel. The cell is then connected to the system and the ground joints made vacuum tight by sealing with Picein wax. The ground joints of the mixing tube are sealed with Picein at the same time. The system is evacuated to $10^{-6}$ mm. and thoroughly flamed. Ammonia gas is then admitted to a pressure of one atmosphere and the system is again evacuated and flamed. Metallic sodium which had previously been sealed into the first bulb of the purification train is then melted through a capillary and distilled through a series of three bulbs. Finally the sodium is distilled into the mixing tube and the distillation train sealed off. No attempt is made to put an exact weight of sodium into the mixing tube. Sodium concentrations are determined analytically from the contents of the cell when the run is completed.

The lower cross tube of the photovoltaic cell vessel is then immersed in refrigerant and dry ammonia is admitted to the system and condensed in the cross tube, thereby dissolving the sodium chloride. The mercury column is used to apply pressure to aid in the condensation of ammonia.

The mixing tube containing the charge of sodium metal is totally immersed in refrigerant and the metal dissolved in liquid ammonia. The photovoltaic cell vessel is now completely immersed in refrigerant while the cooling mixture is removed from the mixing tube. When stopcock *D* is closed, the solution of sodium in liquid ammonia siphons over from the mixing tube into the end chambers of the cell. The well at the junction of the passages to the two end chambers is so designed that approximately equal quantities of solution are sent to each end chamber. The cell is now ready for measurements of the photovoltaic effect.

The source of illumination for the photovoltaic cell is a General Electric Type *H*4 mercury lamp. Radiation above 7,000 Å is filtered out to prevent heating of the sodium solution by infrared. The filter used is a 1 cm. thickness of a 2% aqueous copper sulfate solution contained in a cell with quartz windows.[22] The mercury lamp is enclosed in an inside silvered glass shell which acts as a reflector. Attached to the opening of the reflector is a photographic camera shutter, with a filter holder attached in turn to the shutter. An evacuated glass cylinder, 30 cm. long and 1.5 cm. in diameter, with pyrex optical flats sealed at the ends, is employed to conduct light and maintain a constant distance from the source of illumination to the photovoltaic cell. The illuminating system is lined up above the window *"W"* of the photovoltaic cell (Fig. 2) in such a manner that light passes through the cell chamber and reaches the glass

[22] K. S. Gibson, J. Opt. Soc. Am. **9**, 113 (1924).

bead where the liquid junction between the sodium and sodium chloride solutions is formed.

The following procedure is employed in measuring photovoltaic effects. While the solution is being made up in the cell, the amplifier is allowed to warm up for at least one hour, and the *H*4 lamp is allowed to operate for at least five minutes in order to reach a constant intensity. Meanwhile the dark potential between the electrodes of the photovoltaic cell is determined with the Wolff potentiometer and the Leeds & Northrup thermionic amplifier. In most cases the dark potential between the electrodes is approximately zero.

The electrodes are then switched to the input of the amplifier and the amplifier-oscillograph system adjusted to bring the output corresponding to the value of the dark potential between the electrodes to the center of the oscillograph camera. The camera motor is started and the dark potential is recorded for 30 seconds. The shutter on the light source is opened and the electrode illuminated for one minute, following which the shutter is closed and the decay of the photopotential followed for 1.5 minutes. The camera motor is then stopped.

Films are developed by standard darkroom procedures. The deflections on the film are measured to the nearest tenth of a millimeter with a comparator and converted to millivolts potential change by reference to the calibration curve.

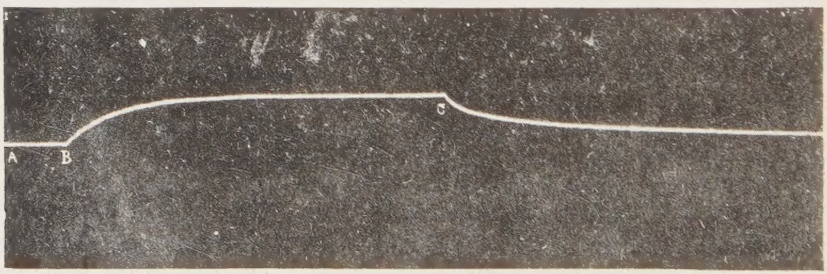


FIG. 3. Typical film record of the photovoltaic effect for a silver electrode in aqueous silver nitrate solution. *A* to *B* dark potential. At *B* one electrode illuminated. At *C* illumination cut off.

In order to demonstate the type of result given by the apparatus, a typical film record of the photovoltaic effect for a silver electrode in aqueous silver nitrate solution is reproduced in Fig. 3. From *A* to *B* the dark potential between the two identical silver electrodes is recorded. At *B* one electrode was illuminated and the rise in the curve indicates the change in potential characteristic of the photovoltaic effect. After one minute of illumination the light was cut off at *C*. The remainder of the curve represents the decay of the photopotential.

## EXPERIMENTAL RESULTS

| Na in $NH_3$ (dark) | NaCl in $NH_3$ | Na in $NH_3$ (illuminated) |
|---|---|---|

In the investigation of the cell seven runs were made. Sodium concen-

trations in the end chambers varied from an opaque dark brown, nearly saturated solution to a dilute, pale blue, transparent solution; or, from about 10 *M* down to about 1 *M*. The concentration of sodium chloride in the middle chamber was about 0.05 *M*. Similar experiments were run on the cell

$$\text{Na in } NH_3 \text{ (dark)} \quad | \quad \text{Na in } NH_3 \text{ (illuminated)}$$

In no case, with either type of cell, when water was completely absent from the system, was a measurable photovoltaic effect observed. In one run the sodium chloride used in the middle chamber was not fused beforehand and therefore introduced a slight amount of water into the cell. For this one cell, photovoltaic effects, erratic in magnitude and sign, were observed. Photopotentials were as high as 20 mv. and might be positive or negative in successive exposures of one minute or less. The photovoltaic effect for this cell disappeared as the sodium was destroyed in the course of 2 hours and the solution in the end chambers became colorless with the formation of a white precipitate. This precipitate was probably sodium hydroxide plus sodium amide.

The anhydrous nature of the liquid ammonia solutions prepared in all other runs was proven by their stability. The sodium solutions retained their characteristic color for at least 3 days; at the end of this period the run was usually terminated.

## DISCUSSION

Among contemporary students of the photovoltaic effect the consensus has been that, for metallic electrodes, photovoltaic effects are caused by emission of electrons from the electrodes.[5]

In the present research a system was used which, according to theory, should show whether or not a photoelectric emission phenomenon will produce a photovoltaic effect. An electrode was used which is known to emit electrons when illuminated, but in no instance was a photovoltaic effect observed. Several possible explanations may be advanced for the absence of a photovoltaic effect in these systems.

The work of Ogg, Leighton and Bergstrom[23] has shown that for solutions of sodium in liquid ammonia in the visible and near ultraviolet regions, there is no photochemical reactions generating products which could influence the electrode potential.

Gibney and Dole,[6] in discussing the absence of a photovoltaic effect for a metallic sodium electrode in a solution of sodium iodide in an aliphatic amine suggest that the difference in electronic energy levels between the metal and solvated positive ions may be too great for the electron to make the transition from metal to solution. In the present case, however, it seems reasonable to assume that the difference between energy levels of electrons in a solution of sodium in liquid ammonia and in a solution of sodium chloride in liquid ammonia is not very large, and that short wave length radiation should give the electron sufficient energy to overcome any small barrier which might exist.

Since it is most probable that electrons are emitted under the experimental conditions, one must conclude that the emission of electrons alone is not sufficient to cause photovoltaic effects for metallic electrodes.

[23] J. Am. Chem. Soc. **55**, 1754 (1933); **56**, 318 (1934).

**Resumen del artículo: "La Emisión de Electrones y el Efecto Fotovoltaico"**

Ultimamente va adquiriendo importancia el estudio del mecanismo del efecto fotovaltaico, por causa de su relación con teorías de electrodeposición. Por eso se describen aquí investigaciones sobre electrodos formados de sodio metálico disuelto en amoníaco líquido. El electrólito era una solución de cloruro sódico en amoníaco.

Se sabe que estos electrodos emiten electrones al iluminarse, y sin embargo no se pudo observar ningún efecto fotovoltaico. Por esto parece que emisión fotoeléctrica no basta para causar efectos fotovoltaicos en electrodos metálicos en contacto con sus iones.